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(54) Title: PROCESS FOR THE PREPARATION OF 1,1,1,3,3-PENTAFLUOROPROPANE

(57) Abstract

This invention is related to the preparation of hydrofluorocarbons (HFCs). Specifically, it relates to the manufacture of 1,1,1,3,3-pentafluoropropane,  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  (HFC-245fa) by the steps comprising (1) the formation of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  by the reaction of  $\text{CCl}_4$  with vinylidene chloride; (2) the conversion of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  by reaction with HF in the presence of a fluorination catalyst, selected from  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  or mixtures thereof; and (3) reduction of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ .

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## PROCESS FOR THE PREPARATION OF 1,1,1,3,3-PENTAFLUOROPROPANE

### BACKGROUND OF INVENTION

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This invention is related to the preparation of hydrofluorocarbons (HFCs). Specifically, it relates to the manufacture of 1,1,1,3,3-pentafluoropropane,  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ , which is referred to in the art as HFC-245fa.

15

HFCs are of current interest due to their potential to replace ozone depleting CFCs and HCFCs which are used in a variety of applications including refrigerants, propellants, blowing agents, and solvents. The compound  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  has physical properties, including a boiling point of about 14°C, which makes it particularly attractive as a blowing agent or propellant. Its ability to function in a manner similar to CFC-11 ( $\text{CCl}_3\text{F}$ , bp 24°C), a well known aerosol propellant at the time, was noted by Smith and Woolf in U.S. Patent 2,942,036 (1960). Ger. Offen, DE 3,903,336, 1990 (EP 381 986 A) also states (using a generic formula) that  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  may be used as a propellant or blowing agent. The use of HFC-245fa as a heat transfer agent is also mentioned in Jpn. Kokai Tokyo Koho JP 02,272,086 (Chem. Abstr. 1991, 114, 125031q).

1,1,1,3,3-Pentafluoropropane was first made by the reduction of  $\text{CF}_3\text{CCl}_2\text{CF}_2\text{Cl}$  over a palladium catalyst (Smith and Woolf, U.S. Patent 2,942,036, 1960). Materials exiting the reaction zone including  $\text{CF}_3\text{CH}_2\text{CHF}_2$ ,  $\text{CF}_3\text{CH}=\text{CF}_2$ ,  $\text{CF}_3\text{CCl}=\text{CF}_2$ , and unreacted starting material. The desired  $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$  was formed in yields up to about 60%, but the source of the starting material was not disclosed. Reduction of 1,1,1,3,3-pentafluoropropene was disclosed by Knunyants et al. (Chem. Abstr., 1961, 55, 349f). The yield of pentafluoropropane was 70%. The only other preparation of  $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$  we are aware of, is its formation, in low yield,

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during the elemental fluorination of tetrahydrofuran (Burdon et al., J. Chem. Soc., C, 1969, 1739).

It is the object of this invention to provide a means of manufacturing 1,1,1,3,3-pentafluoropropane which is economical and amenable to large scale, using readily available raw materials. The process of this invention involves three basic steps, of which any step or combination thereof is novel in the art.

The three steps of the process of this invention are as follows:

- 15        1) the formation of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  by the reaction of  $\text{CCl}_4$  with vinylidene chloride;
- 2) the conversion of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  by reaction with HF in the presence of a fluorination catalyst, selected from  $\text{TiCl}_4$ ,  $\text{SnCl}_4$  or mixtures thereof ; and
- 3) reduction of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ .

Each step is conducted under process conditions ,i.e. temperarture and pressure, sufficient to produce te desired product as discussed herein.

### DETAILED DESCRIPTION

The telomerization of vinylidene chloride by reaction with  $\text{CCl}_4$  is known in the art and has been studied in some detail. The telomerization reaction produces compounds of the formula  $\text{CCl}_3(\text{CH}_2\text{Cl})_n\text{Cl}$ , where n varies as needed for the products desired. The telomerization of vinylidene chloride can be initiated by several means, but initiation with metal salts, particularly of copper, has distinct advantages for the process of this invention. The copper salts are believed to initiate the reaction by first reacting with  $\text{CCl}_4$  to produce a trichloromethyl radical which then combines with vinylidene chloride, initiating the telomerization (see for

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example, Assher and Vofsi, J. Chem. Soc., 1961, 2261 for a discussion of  
5 the mechanism). The copper salts also terminate the telomerization by  
chlorine atom transfer to the growing radical chain. Thus, the chain lengths  
are shortened considerably, compared to e.g. peroxide initiated  
10 telomerizations. For the reactions of interest here, telomers having 3 to 9  
carbon atoms are obtained in excellent yield. Some control of the telomer  
distribution is feasible by controlling the reaction conditions, notably the  
ratio of CCl<sub>4</sub> to vinylidene chloride and the type of copper salt used (see for  
example Belbachir et al., Makromol. Chem. 1984, 185, 1583-1595). Thus  
it is possible to obtain CCl<sub>3</sub>CH<sub>2</sub>CCl<sub>3</sub> with very little higher molecular weight  
telomers (see Example 1).

15 A variety of catalysts have been used in telomerization processes.  
To a large degree, many of these telomerization catalysts, including  
mixtures thereof, can be equivalent, and the choice of catalyst depends on  
cost, availability, and solubility in the reaction medium. For the  
20 telomerization reaction of this invention, it was discovered that salts of  
copper and iron are preferred. Overall, for the reaction of interest here, the  
more preferred catalysts are cuprous chloride, cupric chloride, or mixtures  
of the two or cuprous iodide. The amount of catalysts used in the  
telomerization reaction is at least about 0.1 mmol, and preferably, about  
25 0.1 to about 50 mmol, per mole of saturated halogenated hydrocarbon  
(e.g., CCl<sub>4</sub> or CCl<sub>3</sub>CH<sub>2</sub>CCl<sub>3</sub>) used. At very low concentrations, the reaction  
rate may be unacceptably slow, and very high catalyst concentrations may  
be wasteful due to the fact that the solubility limit may have been reached  
at even lower catalyst to CCl<sub>4</sub> ratios. Consequently, the more preferred  
30 amount of catalyst is about 1 to 20 mmol, per mole of saturated  
halogenated hydrocarbon.

It is also noted that a co-catalyst can be used in the telomerization  
process. Amines may be employed as co-catalysts, preferably in  
35 concentration of 1 to 10 moles per mole of metal catalyst (i.e. copper salt).  
Such amine co-catalysts include alkanol amines, alkyl amines and aromatic

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amines, for example ethanolamine, butyl amine, propyl amine, benzylamine, pyridine and the like.

The ratio of  $\text{CCl}_4$  to vinylidene reactant will substantially alter the degree of polymerization ,i.e. average value of n for compounds of the

5 formula  $\text{CCl}_3(\text{CH}_2\text{Cl})_n\text{Cl}$  . Thus, for example, if the desired product has only one more  $-\text{CH}_2\text{CCl}_2-$  unit than the starting material, the ratio of  $\text{CCl}_4$  (or  $\text{CCl}_3\text{CH}_2\text{CCl}_3$ ) to vinylidene chloride should be relatively high (at least about 2, and preferably, about 2 to 5), so that higher molecular weight telomers are minimized. If the desired product has two or more  $-\text{CH}_2\text{CCl}_2-$  units than  
10 the starting material (e.g.  $\text{CCl}_3(\text{CH}_2\text{CCl}_2)_2\text{Cl}$  from  $\text{CCl}_4$ ), smaller ratios of  $\text{CCl}_4$  to vinylidene chloride (about 0.3 to 1) should be used. The same rationale is used for a system employing vinylidene fluoride.

Useful temperatures for the telomerization reaction range from about

15 25 to about 225°C, preferably 80 to about 170°C, so that, depending on reactant concentrations and catalyst activity, convenient reaction times will vary from a few hours to about one day. More preferred temperatures are in the 125 to 140°C range.

20 Finally a variety of solvents can be used. Any solvent which is inert to the reactants and the desired product can be used. Illustrative of such are acetonitrile, dimethylsulfoxide, dimethylformamide, tetrahydrofuran isopropanol, and tertiary butanol. We prefer acetonitrile due to its low cost, stability, easy recovery via distillation, and ability to dissolve sufficient  
25 amounts of inorganic catalyst salts. Primarily for the latter consideration, the amount of solvent is preferably from about one fourth to two thirds of the total volume, and more preferably one third to one half of the total volume. Otherwise, the amount of dissolved catalyst may be relatively low, or the output of product per run will be adversely affected due to a dilution  
30 effect.

In the second step,  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  is fluorinated to provide  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ . Previously,  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  has been prepared, along with  $\text{CF}_2\text{CICH}_2\text{CF}_2\text{Cl}$ , by fluorination of  $\text{CCl}_3\text{CH}_2\text{CF}_2\text{Cl}$  with antimony halides

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(Chem. Abstr., 1981, 94:174184u). This method, however, is unsuitable for large scale manufacture due to the cost of the fluorinating agent. The preparation of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  by the  $\text{BF}_3$ -catalyzed addition of HF to  $\text{CF}_3\text{CH}=\text{CFCl}$  is also known (R.C. Arnold, U.S. Patent 2,560,838; 1951),

- 5 but the source of  $\text{CF}_3\text{CH}=\text{CFCl}$  was not disclosed. We have also found that HF alone or gave relatively low yields of the desired  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ .

Surprisingly, fluorination (of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$ ) with HF in the presence of either  $\text{TiCl}_4$ , or  $\text{SnCl}_4$  as catalysts can provide the desired  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  in 10 synthetically useful yield. Due to the temperature required for this reaction about (75 to 175°C, and, more preferably, 115 to 135°C,) the reactions are conducted under pressure. The pressure may be controlled by release of by-product HCl, during the reaction process in order to provide a margin of safety if needed depending on the limitations of the equipment being 15 used. We have found it convenient to operate at pressures of about 150 to 500 psig. The upperlimit for pressure is generally a limitation of the available equipment. The reactor consisted of a stirred autoclave fitted with a packed column attached to a condenser maintained at 0 to -20°C. Excess pressure (HCl) is vented through a valve at the top of the condenser into a 20 scrubber. At the end of the heating period, the product and remaining HF are vented through a valve on the autoclave head, which in turn is connected to an acid scrubber and cold traps to collect the product. Under fluorinated materials, such as  $\text{CF}_2\text{ClCH}_2\text{CF}_2\text{Cl}$  may be recycled along with  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  in subsequent batch runs.

25

While both  $\text{TiCl}_4$  and  $\text{SnCl}_4$  gave similar yields of the desired  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ ,  $\text{TiCl}_4$  is preferred due to its lower cost, lower toxicity, and availability in bulk.

30

The mole ratio of HF to organic should be about 4/1 to about 20/1, preferably 5/1 to about 9/1. Since over-fluorinated material,  $\text{CF}_3\text{CH}_2\text{CF}_3$ , is generally not desired, it is more advantageous to allow more under-fluorinated material (which can be recycled) in the crude product. Over-fluorinated product is keep low by smaller HF/organic ratios and lower

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reaction temperatures. The reaction temperatures range from 75 to about 150°C, while the preferred temperatures range from about 115 to about 135°C. Under these conditions, the reaction times range from about one to about 25 hours, and can be monitored by the rate of pressure (HCl)

5 increase.

In the last step,  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  is reduced to 1,1,1,3,3-pentafluoropropane, which is unknown in the art. The reduction can be conveniently accomplished in a continuous flow system by passing vapors 10 of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ , along with hydrogen, over a catalyst.

The latter include nickel, palladium, platinum and rhodium, which are usually supported on inert materials, such as carbon or alumina. These catalysts are available commercially and generally can be obtained having 15 0.5 to 20% by weight of the metal on the support material. More commonly, loadings of 0.5 to 5% weight percent are employed. Examples include 1% palladium on activated carbon granules and 0.5 % platinum on 1/8" alumina pellets. The more preferred catalyst is palladium due to its lower cost compared to either platinum or rhodium.

20

While it is most convenient to operate to atmospheric pressure, this is not required. Both subatmospheric pressures or pressures up to 100 atmospheres may be used, the latter especially in batch operations.

25

In the fluorination step it may be preferable to utilize a solvent, such as methanol, ethanol and acetic acid. A base may also be beneficial to neutralize the HCl produced. Any neutralizing agent can be used, e.g. sodium hydroxide, potassium hydroxide, sodium acetate and sodium carbonate.

30

Useful temperatures for vapor phase reductions range from about 100 to 350°C, more preferred ranges are 150 to 250°C.

35

Based on reaction stoichiometry, the required ratio of hydrogen to organic is 1 mole of organic is 1 mole of hydrogen per mole of organic.

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From 1 to about 50 times the stoichiometric ratio may be used. A ratio of 2  
5 to 30 times the stoichiometric amounts can be used with satisfactory  
results.

The most desirable conditions for the reduction will vary and will  
depend, in part, on the activity of the catalyst (which depends on the type  
10 of metal used, its concentration on the support material, and the nature of  
the support material), and the contact or residence time in the reactor.  
Residence times may be adjusted by changing the reaction temperature, the  
catalyst volume, and the flow rates of hydrogen and/or organic material to  
be reduced. Useful contact times range from about 0.1 sec to about 2  
15 minutes. In the present case, more preferred contact times range from  
about 10 to 40 seconds at 200-225°C and atmospheric pressure.

In the reduction of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  at atmospheric pressure and at  
temperatures of about 100 to 325°C, both  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  and  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$   
20 are generally present in the reactor effluent stream. The ratio of  
 $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  increases with increasing reaction temperature.  
Continuous operation at high temperatures (>250°C) is not very  
advantageous, due to potential gradual loss of the original catalyst activity.  
Consequently, the preferred method to achieve relatively high conversions  
25 of  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  to  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  is to increase the contact time, or  
equivalently, to recycle the product stream until the desired conversion is  
obtained. After separating the desired  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  from  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ , the  
 $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  may be fed into the reactor again.

30 **Example 1 - Preparation of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$**

A teflon-lined, magnetically stirred autoclave (575 mL capacity) was  
charged with 150 mL  $\text{CCl}_4$ , 150 mL  $\text{CH}_3\text{CN}$ , 0.51 g  $\text{CuCl}$  and 0.51 g  $\text{CuCl}_2$   
35 dihydrate. The autoclave was closed and evacuated briefly. Vinylidene  
chloride (57.7g, 0.595 mol) was added via syringe and a rubber septum  
over a ball valve on the autoclave. The autoclave was then pressurized  
with nitrogen to 20 psig at room temperature. The mixture was heated

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over 1.75 h to 150°C and maintained at 150°C for 2 h. The stirrer speed  
5 was maintained at 350 rpm. After cooling the autoclave and contents to  
about 15°C, the contents were removed, diluted with 400 mL water, and  
the organic layer separated. The aqueous layer was extracted with 50 mL  
methylene chloride, and the combined organic layers washed with 100 mL  
brine. After drying ( $\text{Na}_2\text{SO}_4$ ), the organic layer was concentrated by rotary  
10 evaporation to give 140.4 g crude product. Distillation at 2.7 mm Hg gave  
114.3g  $\text{CCl}_3\text{CH}_2\text{CCl}_3$ , bp 63-65°C (77% yield based on vinylidene chloride  
added). Its purity by GC analysis was 99.97%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): singlet  
at 4.17  $\delta$ .

**15 EXAMPLE 2 HF Fluorination with  $\text{TiCl}_4$**

A 600 mL, magnetically stirred, model autoclave fitted with a  
condenser (maintained at -10°C), was evacuated, cooled to about -40°C,  
and charged with .6.9 g (0.036 mol)  $\text{TiCl}_4$  followed by 64 g (0.255 mol)  
20  $\text{CCl}_3\text{CH}_2\text{CCl}_3$ , and 102.5 g (5 mol) HF. The temperature was increased to  
120°C and maintained at that temperature for a total of 22 h. During the  
heating period, pressure in excess of 400 psig was periodically vented to an  
aqueous KOH scrubber which was attached to two -78°C cold traps. At the  
end of the heating period, the remainder of the autoclave contents were  
25 slowly vented. The cold traps contained 36.1g material which by GC  
analysis, contained 14.5%  $\text{CF}_3\text{CH}_2\text{CF}_3$  and 84.0%  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ ,  
corresponding to a yield for  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  of 69%.

**30 EXAMPLE 3 - HF Fluorination with  $\text{SnCl}_4$**

In the manner and apparatus described in Example 2, 63.5 g  
 $\text{CCl}_3\text{CH}_2\text{CCl}_3$ , 101.4 g HF, and 13.5 g (0.052 mol)  $\text{SnCl}_4$  were heated to  
125°C for 23.5 h. The cold trap contained 41.5 g material, which by GC  
35 analysis contained 13.4%  $\text{CF}_3\text{CH}_2\text{CF}_3$ , 66.3%  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ , and 20.3%  
 $\text{CF}_3\text{CH}_2\text{CFCl}_2$ , corresponding to a yield for  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  of 65%. The crude  
products from Examples 3 and 4 were combined and distilled to give 99.4%

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pure (GC)  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ , bp 27-30°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.2 tq ( $J = 9$  and 5 Hz).

#### EXAMPLE 4 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ - at 200°C

The reactor used in this Example consisted of an electrically heated glass column containing a catalyst bed comprised of a mixture of 10 cc 1% Pd on activated carbon (4-8 mesh) and 15 cc glass helices. Hydrogen was passed over the catalyst at 140 cc/min and  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  was introduced at a rate of 2.25 g/h. The reaction temperature was 200°C. The material exiting the reactor was collected in a cold trap and consisted of approximately 1/3  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$  and 2/3 unreacted  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  by GC analysis.

#### EXAMPLE 5 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ at 225°C

Example 4 was repeated, except that the reaction temperature was increased to 225°C. The volatile material which collected in the cold trap consisted, by GC analysis, of 51%  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ . The remainder was primarily unreacted  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ . Distillation gave  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ , bp 14°C. the recovered  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  was recycled to provide additional  $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ .

#### EXAMPLE 6 - Reduction of $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ at room temperature

An autoclave was charged with a solution of 10 g KOH in 60 mL methanol, 0.5 g 1% Pd on carbon, and 25 g (0.15 mol)  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ . Stirring was begun and the autoclave pressurized to 250 psig with hydrogen. After 20 hours, the contents were cooled to 0°C and excess hydrogen was bled off. The remaining volatile organic material was then transferred to a cold receiver under vacuum. Distillation of the crude material so obtained gave  $\text{CF}_3\text{CH}_2\text{CHF}_2$ .

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What is Claimed is:

1. A process for the preparation of 1,1,1,3,3-pentafluoropropane ( $\text{CF}_3\text{CH}_2\text{CF}_2\text{H}$ ) comprising:  
reacting  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  with hydrogen in the presence of reduction catalyst.
2. The process of claim 1 wherein the reduction catalyst is selected from nickel, palladium, platinum and rhodium.
3. The process of claim 1 wherein the  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$  is prepared by the step comprising reacting  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  with HF.
4. The process of claim 3 further comprising the step of recycling materials produced other than  $\text{CF}_3\text{CH}_2\text{CF}_2\text{Cl}$ .
5. The process of claim 3 wherein the fluorination catalyst is selected from  $\text{SnCl}_4$  and  $\text{TiCl}_4$ .
6. The process of claim 3 further comprising the preparation of  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  by reacting  $\text{CCl}_4$  with vinylidene chloride.
7. The process of claim 6 wherein said process is conducted in the presence of metal catalyst.
8. The process of claim 7 wherein the catalyst is cuprous chloride, cupric chloride, or a mixture thereof or cuprous iodide.
9. A process for the preparation of  $\text{CF}_3\text{HC}_2\text{CF}_2\text{Cl}$  comprising reacting  $\text{CCl}_3\text{CH}_2\text{CCl}_3$  with HF in the presence of a fluorination catalyst selected from  $\text{SnCl}_4$  and  $\text{TiCl}_4$ .

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/08263

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C07C17/23 C07C17/20 C07C17/278 C07C19/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 539 989 (HOECHST AKTIENGESELLSCHAFT) 5 May 1993 see the whole document ---	1,2
X	EP,A,0 522 639 (SOLVAY (SOCIÉTÉ ANONYME)) 13 January 1993 see the whole document ---	3-9
X	US,A,3 651 019 (M. ASSCHER ET AL.) 21 March 1972 see example 9 -----	3-5

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## Special categories of cited documents:

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
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- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

- 'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- 'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- 'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- '&' document member of the same patent family

1:

Date of the actual completion of the international search

2 November 1994

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/US 94/08263

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0539989	05-05-93	CA-A-	2081813	02-05-93
		JP-A-	5221894	31-08-93
EP-A-0522639	13-01-93	BE-A-	1005096	20-04-93
		JP-A-	5201892	10-08-93
US-A-3651019	21-03-72	BE-A-	622939	